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POLYMER INFILTRATION STUDIES

By
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Progress Report
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December 1992

POLYMER INFILTRATION STUDIES

Summary

Significant progress has been made during the past three months on the preparation of carbon fiber composites using advanced polymer resins. The results are set forth in recent reports and publications, and will be presented at forthcoming national and international meetings.

Current and ongoing research activities reported herein include:

- ✓ Powdered Tow Ribbonizing
- Unitape from Powdered Tow
- Customized Towpreg for Textiles and ATP
- Textile Composite Research

During the period ahead research will be directed toward further development of the new powder curtain pregging method and on ways to customize dry powder towpreg for textile and robotic applications in aircraft part fabrication. Studies of multi-tow powder prepregging and ribbon preparation will be initiated in conjunction with continued development of prepregging technology and the various aspects of composite part fabrication using customized towpreg. Also, a major effort during the coming months will be participating in the analysis of the performance of the new solution prepregger.

Polymer Infiltration Studies

The goal of the polymer infiltration investigations is to develop methods by which to produce advanced composite material for automated part fabrication utilizing textile and robotic technology in the manufacture of subsonic and supersonic aircraft. This object is to achieved through research investigations at NASA Langley Research Center and by stimulating technology transfer between contract researchers and the aircraft industry.

The powder curtain prepregging system, which was started up successfully last Summer, is currently undergoing modifications. During the next few weeks, an automated powder return system will be installed and the resin monitoring gamma gauge will be connected to the pull roller of the takeup winder to provide a feedback quality control loop for the unit. These changes should provide better opersting control over fugitive powder and improved towpreg quality control.

Issues in the use of powder coated towpreg for textile applications have been the subject of significant effort. Progress to date was presented at the Fiber-Tex meeting in Philadelphia in October, see attachments. An outline of planned textile composites research has been prepared to guide activities during the next two years, see attachments.

Consideration of the ways to customized towpreg for use in automated tow /fiber placement has resulted in several new approaches and will be the subject of a paper to be presented at the 10th Thermoplastic Matrix and Low Cost Composite Review in February, see attachments. Noteworthy among the ideas that have been developed is the potential benefits from use of non-rectangular ribbon, and the thermal wave bonding model of tow placement with on-the-fly-cure. As described in the attached memoranda, several efforts to produce quality towpreg ribbon are underway. In addition to die forming methods, it is planned to investigate making unitape from powdered tow which can then be slit into the desired ribbon geometry.

Three papers are schedule for presentation at the 38th International SAMPE Symposium & Exhibition next May. The first paper deals with the new powder curtain prepregging method and will be the inital public disclosure of the new process. The second paper describes the new NASA solution pregregger, and the third paper reports on the effect of fiber volume fraction on composite properties.

Attachments

1. Specialized Prepreg Ribbon for Automated Fiber Placement, Memorandum dated November 25, 1992.
2. Towpreg Ribbonizing, Memorandum dated December 21, 1992.
3. Outline of Projects for Textile Composite Activities for FY 93 and FY 94
4. " Issues in the Use of Powder-Coated Towpreg for textile Applications", M. Hugh, J. Marchello, and N. Johnston, presented at FIBER-TEX'92.

November 25, 1992

Memorandum

To: N. Johnston, R. Baucom, J. Nelson, D. Sandusky,
M. Hugh, S. Wilkinson, and J. Hinckley
From: J. M. Marchello *JMM*
Subject: Specialized Prepreg Ribbon for Automated Fiber
Placement

As we discussed during our meeting last Thursday, several approaches are being taken to try to make ATP ribbon, using advanced resins (thermoplastics and toughened thermosets), that has special cross-sections (triangle, trapezoid, parallelogram). Efforts elsewhere (Scot Taylor and John Muzzy) have not yet produced a good quality preconsolidated ribbon of uniform width. On Monday, we made our first run with the "hot shoe" die. As will be discussed later, the results were encouraging, but not a complete success. The purpose of this memorandum is to try to summarize where these efforts stand and what are their directions during the period ahead.

ATP ribbon is currently made by slitting unitape prepreg (epoxy thermoset or APC-2 PEEK thermoplastic). There are four approaches to making towpreg ribbon from powdered fiber tow.

- Pultrude towpreg through a die. This is the approach being investigated by Scot Taylor.
- Pass the towpreg between a set of roller dies. This has been tried here and by John Muzzy.
- Pull the towpreg over an open "hot shoe" die. We have just begun this study.
- Pass powdered tows through our prepregger to make a unitape and slit to desired ribbon shape.

Monday afternoon we pulled powder towpreg made of 12k AS-4 carbon fibers coated with PEEK (40 w%) through the "hot shoe" ceramic die. This was the first test of the die which has a 1/4 inch rectangular channel and is intended for use in making PEEK ribbon for McAir.

During the runs a pulling rate of 6 ft/min was used which means that towpreg residence time in the die hot zone was about 2 seconds. At 705°F the ribbon appeared essentially unchanged. It was 1/4 inch wide and looked the same as the material on the feed spool. At 750°F the

ribbon had contracted to a 3/8th inch width. It was clear that resin had flowed with some accumulation at the top (open) side of the ribbon. A quartz top on the die had been removed because it caused resin buildup and die jamming.

Samples of the ribbon from both the 705 and 750°F pulling runs were taken to obtain micrograph and SEM photographs. Additional tests with this die will be made during the next few weeks. These runs will explore questions such as: Why did the ribbon contract to a width less than that of the die? How can the accumulation of resin on the top side of the ribbon be eliminated? What is the extent of fiber damage? Is the ribbon fully wetted, or are there dry fibers in the center?

As mentioned during our meeting last Thursday, the idea of passing powder coated tows through the prepregger to make unitape should be explored. Ultimately one would want to powder coat on-line, however, until a reliable 12 inch wide powder curtain feeder has been developed, it seems best to powder coat off-line. In regard to making customized ATP tape from slit powder tow unitape there are several issues that need to be resolved:

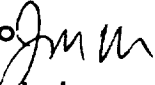
- Can unitape be made from tow that has been coated with powdered thermoplastic resin?
- Can a 12 inch long powder curtain feeder be developed?
- Can Unitape be slit at angles to obtain the ribbon shapes needed for customized ATP tow?

When modifications to the powder curtain unit have been completed, it will be used to make PEEK towpreg for use in addressing the first question. We have been thinking of producing 30 spools, each holding 300 feet of towpreg, as the starting material for the unitape tests. Once we have purchased 12 inch helix screws for the two large powder feeders, the development of the powder curtain sleeves for the screws and their testing can begin in the powder booth. During our visit to American GFM last week we saw ultrasonic cloth and prepreg cutters that can be set at angles to produce the various towpreg ribbon architectures. Acquisition of these type cutters and the development of appropriate mounts for them on the prepregger would begin the resolution of the third question. One additional concern is how best to take up the ribbon?

December 21, 1992

Memorandum

To: N. Johnston, R. Baucom, D. Sandusky, M. Hugh,
S. Wilkinson, and J. Hinkley

From: J.M. Marchello 

Subject: Towpreg Ribbonizing

On December 2, we visited Custom Composites in Atlanta to observe their powder prepregging system and to discuss towpreg ATP ribbonizing with John Muzzy and his students at Georgia Tech. The powder prepregging unit at Custom Composites was operated at 125 ft/min during our visit and seemed to do a good job. Significant amounts of powder are carried over and collected for reuse. This may result in fiber plugging of the feeder over time, since some fibers are usually present in recycled powder. Quality control continues to be an area of concern and they are working on development of an on-the-fly tow ribbon weighing guage.

The students at Georgia Tech have given up on using roller dies for ribbonizing. So have we. They are testing a 3 inch electrically heated pultrusion die. During the discussion, it was suggested that they try operating at higher temperature and consider preheating the entering towpreg to just below T_g . The ribbon, made from a 12k AS4 PEEK tow, that they showed us appeared similar to ribbon being made by Scott Taylor. According to McAir, the main concerns with these ribbons has been dry fibers in the center and loose fibers on the surface which tend to jam the ATP ribbon cutter.

As mentioned in the November 25 memorandum, our current ribbonizing activities deal with using the open hot shoe die. From the results of the initial runs, described in the memorandum, it was clear that something had to be done to keep the ribbon at the 1/4 inch width. Two changes have been made. First was to use two towpregs rather than only one. Second was to reduce the drag, or tension on the tows, by raising the guide bars in front and back of the die, so that the towpreg is not held tightly in the die slot, but simply slides through it.

These approaches produce a good appearing ribbon during short runs on December 11 and 14. It has the desired 1/4 inch width, is about 10 mills thick, and appears similar to silt APC-2. There are differences. The

towpreg has 40 w% resin so the ribbon has a lower fiber volume than APC-2, and it is not as nice an appearing ribbon. SEM photos indicate a resin rich layer in the middle of the ribbon. Since we made it from two ribbons, one on top of the other, a boundary region was expected, but not one with quite as much resin as shown in the SEM photos. The approach of heating from the top and dragging the ribbon bottom over the die may result to resin flow into the ribbon center. This could explain the SEM photographs. The ribbon is of about the same stiffness as APC-2. It does not appear to have loose fibers on the surface, so it may not plug the McAir ATP ribbon cutters.

On December 16 the system, using two towpregs, was continuously operated for a 75 minute interval. The objective was to determine what problems might arise during extended operation, and if possible, to make ribbon for McAir to test. After an initial slow startup the unit was held at a tow speed of 10 ft/min with a die temperature of about 1200°F. During the first thirty minutes the ribbon appeared good, but resin and fibers were observed accumulating in the die. At first this did not seem to be a problem and may actually have reduced die friction, however over time some of the fiber and resin in the die would release and pass out attached as a clump on the ribbon, which had to be picked or cut off.

In the middle of the run we came to a cut in the towpreg on one of the feed spools. Rather than shutdown we managed to feed the cut towpreg through the die hot zone on the fly and return to steady operation in a few minutes. As the one hour mark was approached fiber and resin accumulation became a major problem resulting in necking down of the ribbon and excessive clumps on the ribbon leaving the die. The unit was shutdown after 75 minutes when one of the feed spools ran out of towpreg. Also, early in the run the reversing mechanism on the takeup winder failed, requiring that it be manually reversed at the end of each traverse.

On the basis of the these test runs it is difficult to say whether the hot shoe die approach can be developed as a practical method for producing large quantities of ATP ribbon. The concerns expressed above will need to be addressed in designing a new die for additional tests. Also, as mentioned in the November 25 memorandum, in parallel with this effort, we shall try to use the prepregger to make a tape from powdered towpreg which can then be slit into ATP ribbon.

Outline of Projects for Textile Composite Activities for FY93 and FY94

Frameworking for Unidirectional Composites

Mechanical Properties - Resin Qualification (AMD0036, AMD0029, LARC-TPI)

SBS

Flexure Strength and Modulus

Compression

Tension

Tape Product from Powder Coated Material

Powder coated product as off-line process

Powder coating on-line with tape production

Determine appropriate degree of consolidation needed in tape product to produce well-consolidated panels

Thermal tests to verify state (extent of cure, Tg, etc.) of polymer in tape product

Optical microscope tests to verify state (degree of consolidation, % voids, distribution of polymer, wetting of fibers, etc.) of tape product

Mechanical Properties

Open Hole Tension - quasi-isotropic layup

Open Hole Compression - quasi

Compression after Impact - quasi

Woven 8HS Composites from Powder Coated Towpreg

Produce 8HS fabric from powder coated towpreg yarn

Improve the towpreg yarn for the weaving process

Produce composite panels

Determine appropriate layup for optimal processing

Characterize consolidation of composites with regards to varying V_f

Characterize bulkiness of fabrics

Determine tension and compression strengths and moduli of 8HS composites

Braiding

- Establish braiding protocol for biaxial and triaxial fabrics

 - Improve yarn for braiding process

 - Vary tow sizes

 - Vary resin content, V_f

- Measure tension and compression strengths and moduli as functions of tow size

 - resin content, V_f

- Characterize bulk factor of 2D fabrics

Debulking and Consolidation of 2D (braided and woven) fabrics

- Develop methods for debulking powder-coated preforms

 - Characterize fiber movement

 - Identify point of intimate contact

 - Develop preform debulking tooling

- Develop methods for net shape consolidation

 - Preform stitching

 - Net shape tooling

- Produce three demonstration parts

 - Select geometry of structure

 - Machine tooling for structure

 - Consolidate final part

Issues in the Use of Powder-Coated Towpreg for Textile Applications

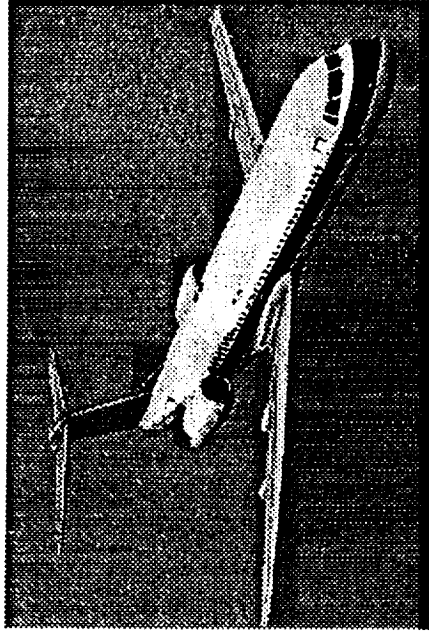
M. K. Hugh and J. M. Marchello
Old Dominion University

N. J. Johnston
NASA Langley Research Center

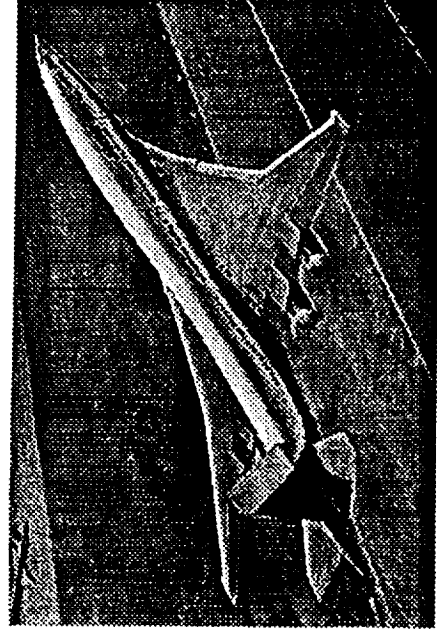
Overview

- **Introduction**
- **Methods of Powder Prepregging**
- **Weaving and Braiding Issues**
- **Weaving and Braiding Solutions**
- **Accomplishments and Future Direction**

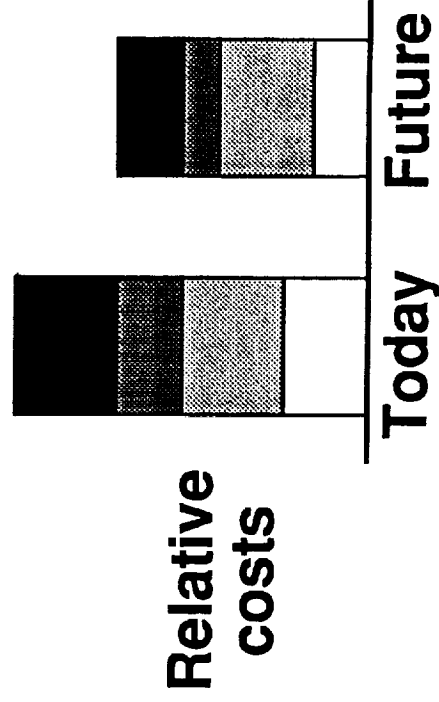
Composites In Aircraft Manufacturing



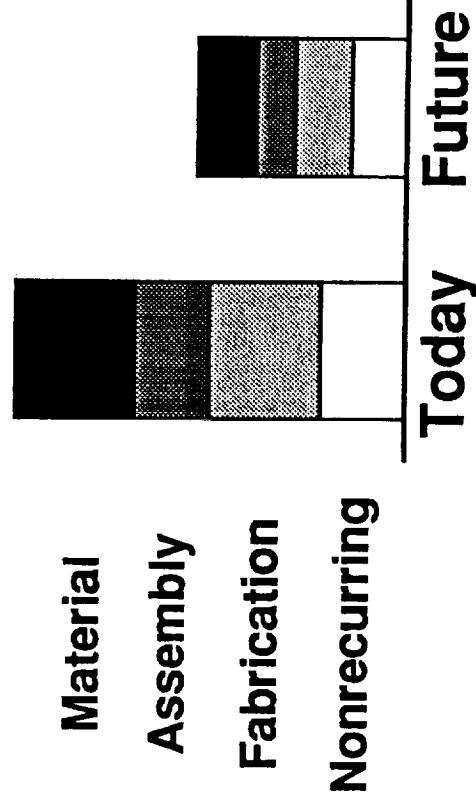
Subsonic



Supersonic



Graphite / Epoxy



Graphite / Thermoplastic

Features of Dry Powder Prepregging

- **Versatile: Thermoplastics and Thermosets**
- **No Solvents**
- **Costs Comparable to SOA Methods**
- **Adaptable to Carbon Fiber Manufacturing Line**
- **Room Temperature Storage of Towpreg**
- **Tailorable**
- **Alternative to RTM**

Powder-Coated Towpreg Technology

Some Key Organizations

Government

- **NASA Langley Research Center and Old Dominion University**

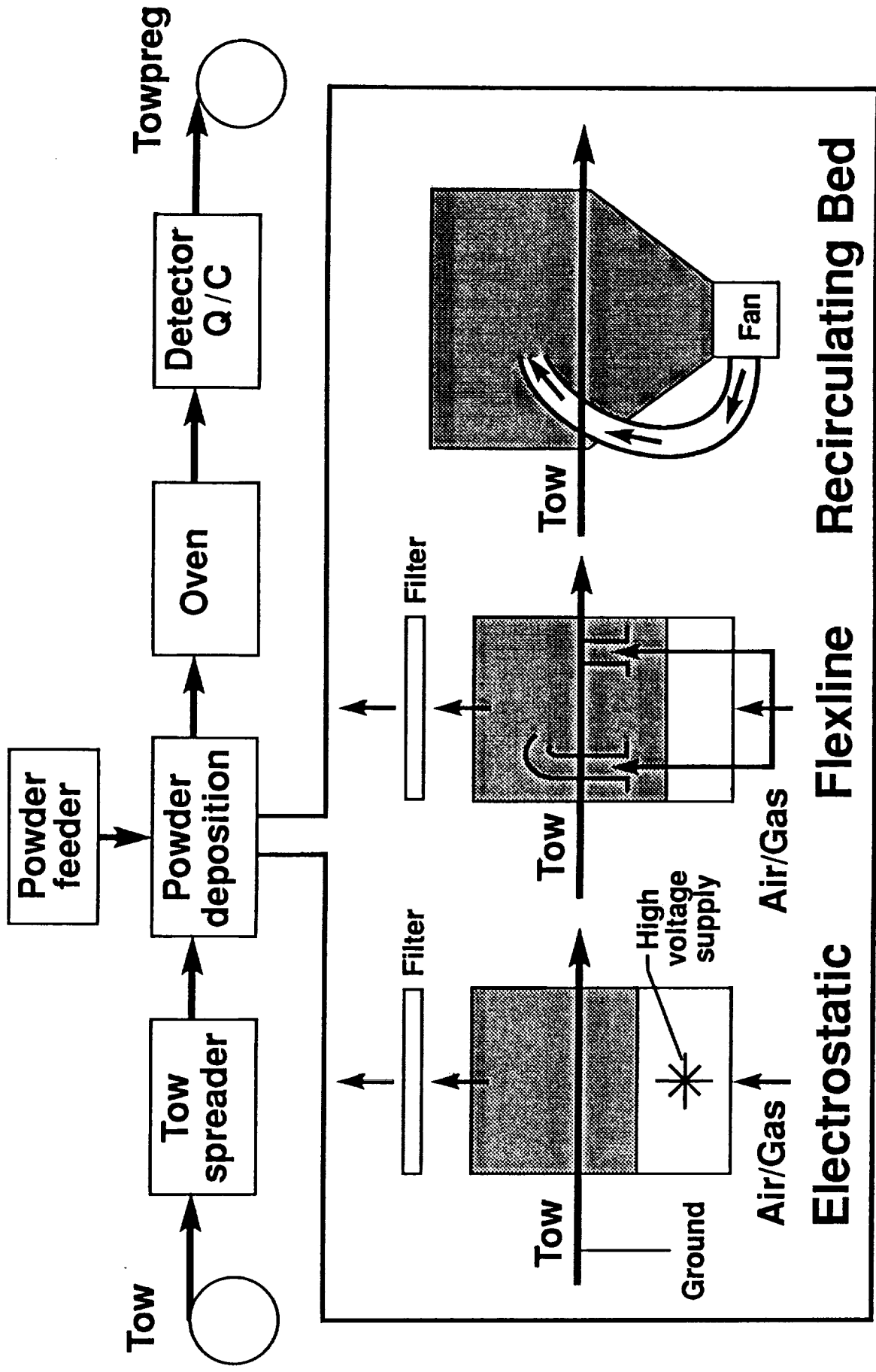
Commercial Industries

- **BASF Structural Materials, Inc.**
- **Custom Composites Materials, Inc. and Georgia Tech**
- **Electrostatic Technologies**
- **Flexline B. V.**
- **Enimont and Ciba Geigy**

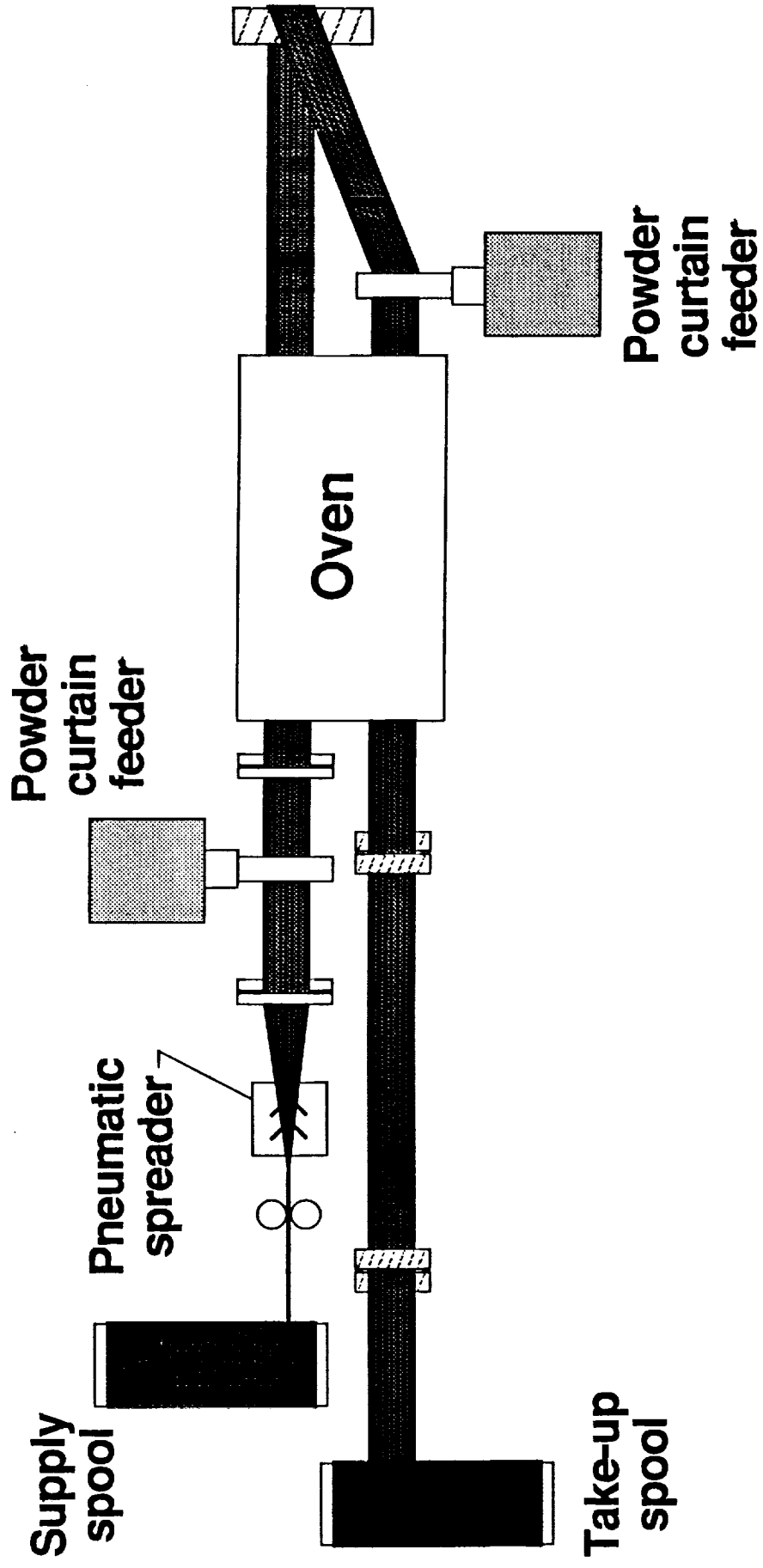
Universities

- **Clemson University**
- **Michigan State University**
- **Virginia Polytechnical Institute**

Dry Powder Towpreg Systems



LaRC Powder Coating Schematic



Prepregging Materials

Carbon Fibers

Unsize 3k, 6k, 12k

AS-4 (Hercules)

G30-500 (BASF)

IM-7 (Hercules)

Polymer Powders

Particles sizes from 1-50 μm

Thermoplastics

LARCTMTPI (Mitsui Toatsu)

PEEK (ICI)

PEKK (DuPont)

PiSO₂ (HiTech Services)

Thermosets

Compimide T-2 (Shell)

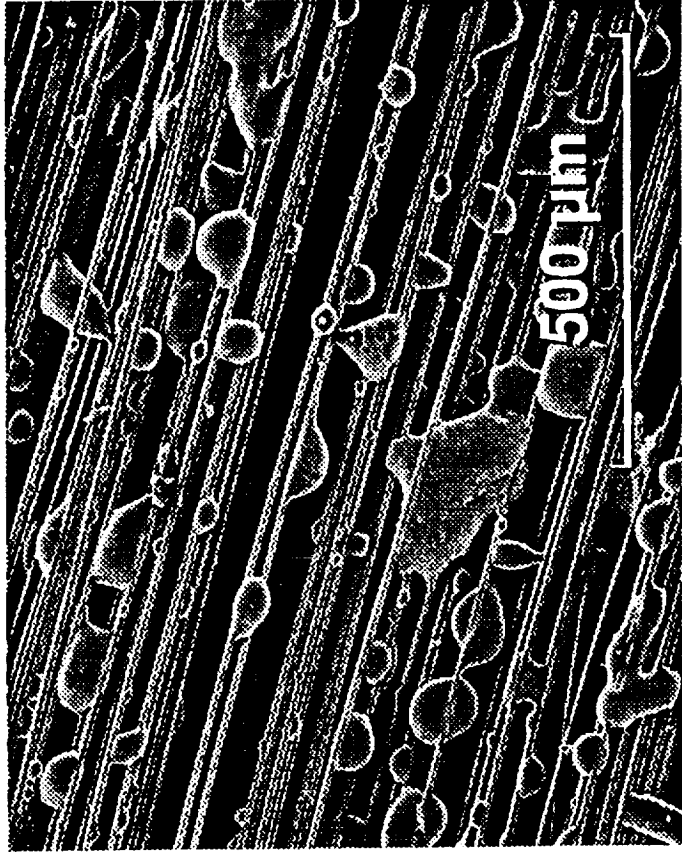
RSS1952 (Shell)

CET-3 (Dow)

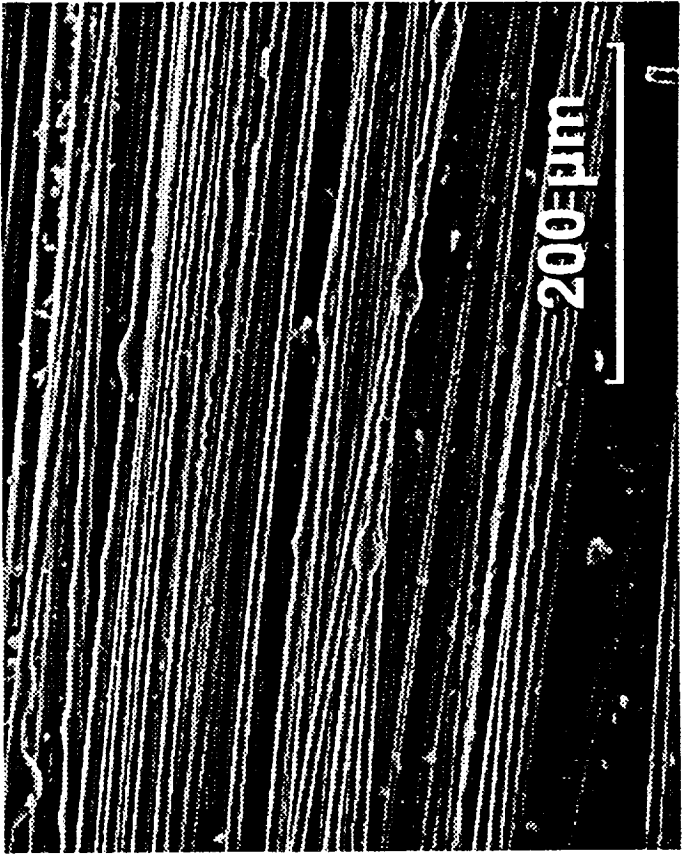
**PR500 experimental epoxy
modifications (3M)**

**PMR-15 polyimide modifications
(NASA LaRC)**

Scanning Electron Micrographs Of Dry Powder Coated Towpreg



Thermoplastic Polyimide
(LARC™-TPI) on
Carbon Fiber (AS-4)



Epoxy (PS-500) on
Carbon Fiber (AS-4)

Mechanical Properties of Unidirectional Thermoplastic/AS-4 Composites

	Powder Prepreg		Hot-Melt Prepreg
	LARC TM TPIMF	LARC TM TPIH ^F	APC-2*
Flexural strength (ksi)	255 ± 15	264 ± 14	290
Flexural modulus (Msi)	15.6 ± .3	15.7 ± .6	18
Interlaminar shear strength (ksi)	13.4 ± .8	—	18
Transverse flexural strength (ksi)	23.1 ± 1.8	—	—

* Data obtained from ICI Fiberite Materials Handbook.

Weaving and Braiding Issues

- Resin
 - Thermoplastic
 - Thermoset
- Surface Characteristics
 - Coating
 - Damage
- Cross-Sectional Shape
 - Rectangular
 - Circular
- Bulk
- Flexural Rigidity

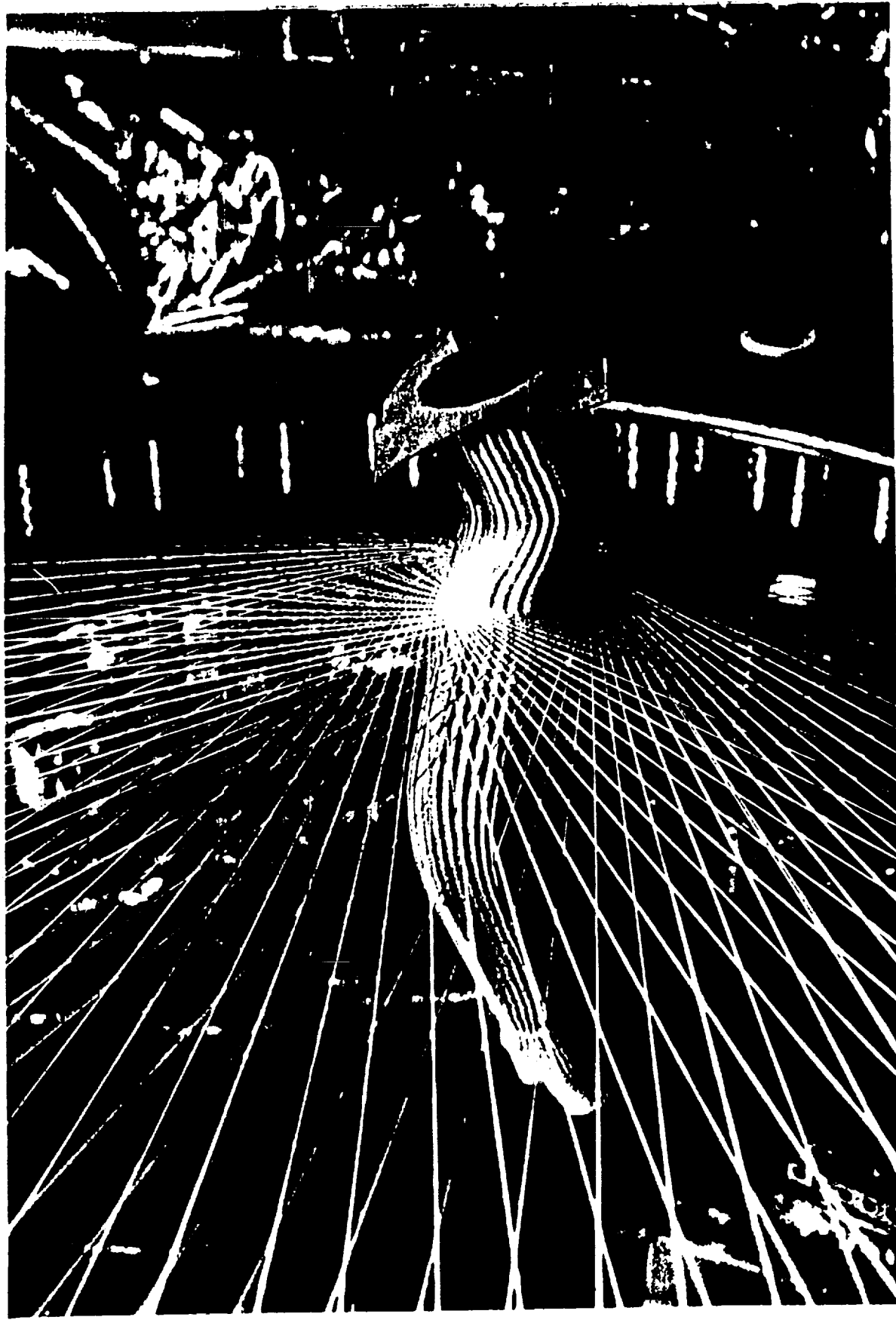


Warp

Fill

L-90-2855

2-D BRAIDED TURBO JET ENGINE INLET DUCT



Weaving and Braiding Solutions

- **Twisting**
15 tpm (.4 tpi) - 79 tpm (2 tpi)
- **Serving**
Polymer Monofilament
- **Glazing**
- **Water Treatment**

Effects of Customized Towpreg on Weaving & Braiding

	Water	Twist	Serving	Glazing
Surface	Lubrication	Uniform	Uniform	Uniform
Shape	–	Circular	Circular	Circular-Rectangular
Bulk	–	Reduced	Reduced	Reduced
Flexibility	Increased	?	?	Tailorable

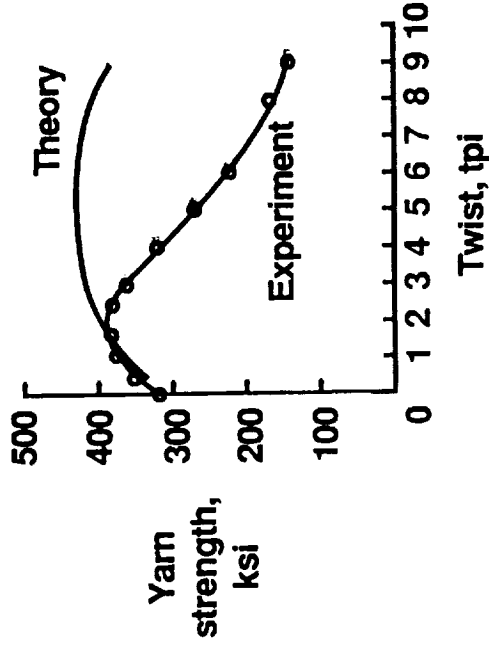
Towpreg Weaving Conditions

Subcontractor: Textile Technologies, Inc.

- **Rewinders**
 - Server Machine, Cross Wind Pattern, 5 cm Dia Cores (2"D)
 - Ruff Winder Machine, Parallel Wind Pattern, 5 cm Dia Cores (2"D)
- **Loom**
 - Iwer 1200 Loom, Capable Speeds up to 100 ppm
 - Actual speed of 40 ppm
- **Weave Pattern**
 - Eight Harness Satin, Balanced Fabric
 - 12k lot - 8 x 8 ppi
 - 6k lot- 10 x 10 ppi
 - 3k lot- 20 x 20 ppi

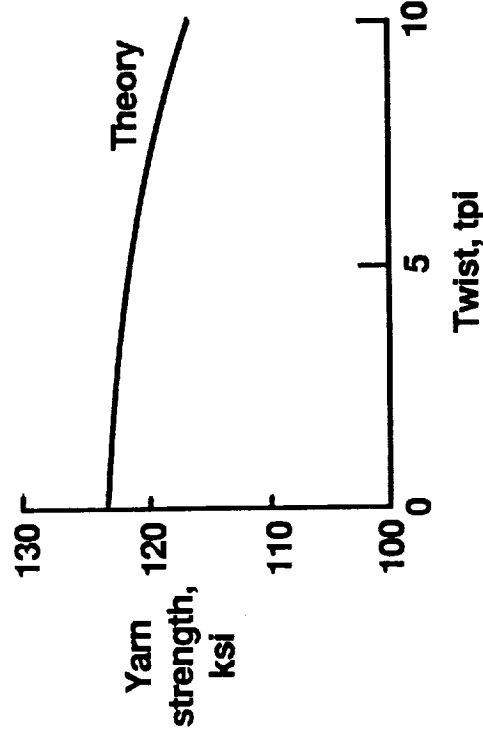
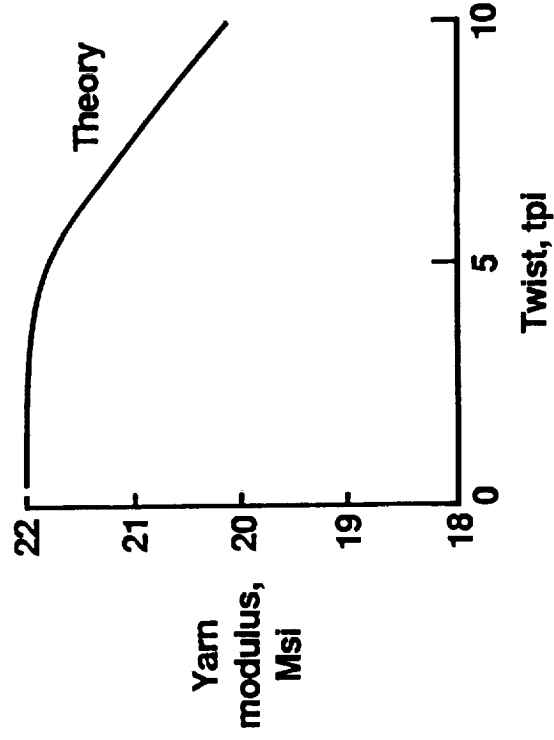
Literature Survey in Twisted Yarn Mechanics

Zweben, Smith, Wardle (1979)
- Yarn strength peaks at 2 tpi



Whitney (1966)

- 5 tpi is not detrimental to graphite reinforced composites

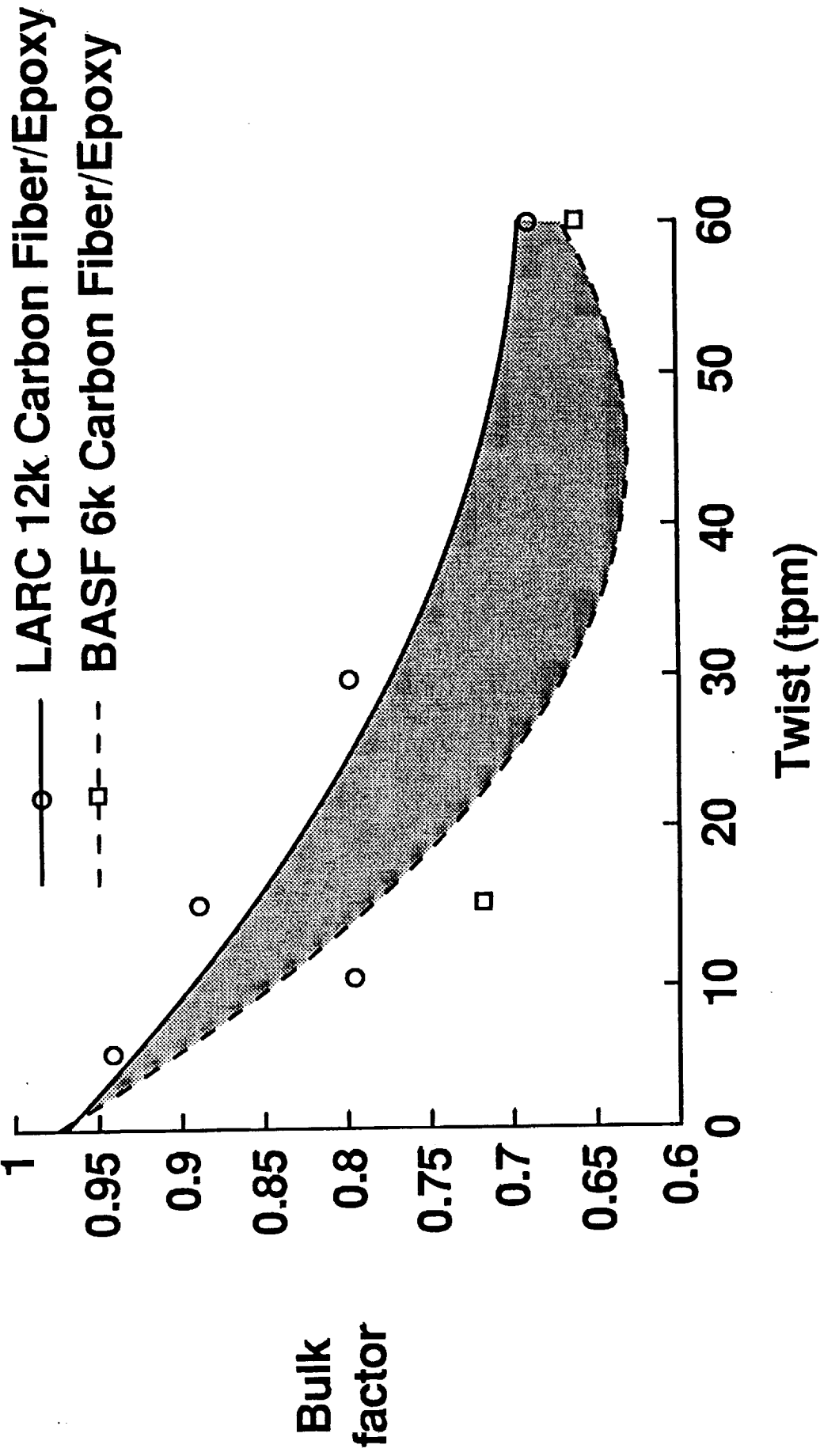


Mechanical Properties of Unidirectional 12k AS-4/LARC™TPI MF

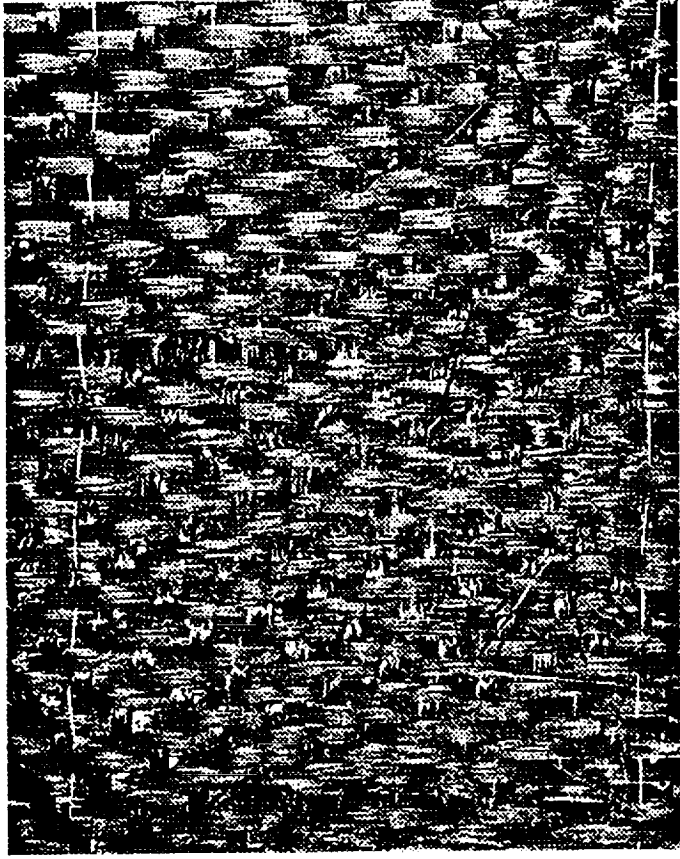
	Non-twisted towpreg	Twisted towpreg (15 tpm)
Compressive strength (ksi)	165 ± 4	140 ± 10
Compressive modulus (Msi)	17.1 ± .8	15.7 ± .9
Poisson's ratio	.345 ± .023	.382 ± .030
Interlaminar shear strength (ksi)	13.4 ± .8	15.2 ± 1.0
Flexural strength (ksi)	255 ± 15	249 ± 16
Flexural modulus (Msi)	15.6 ± .3	16.2 ± .4

Towpreg Bulk Factor vs. Twist

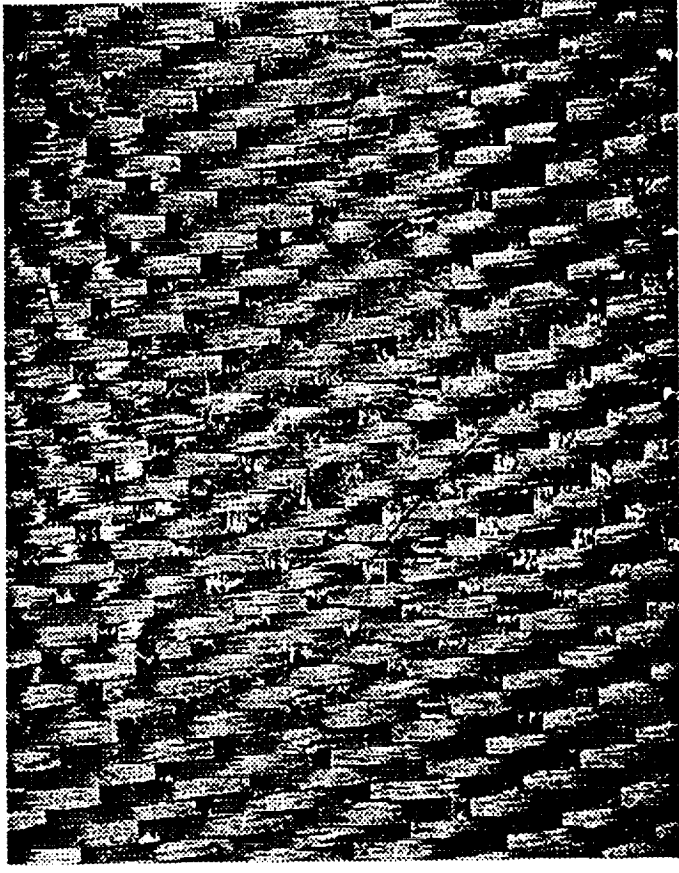
$$\text{Bulk Factor} = \frac{\text{Area Twisted Towpreg}}{\text{Area Untwisted Towpreg}}$$



Photographs Of Eight Harness Satin Woven Cloth From 6k Carbon Fibers And LARC™ -TPI Powder

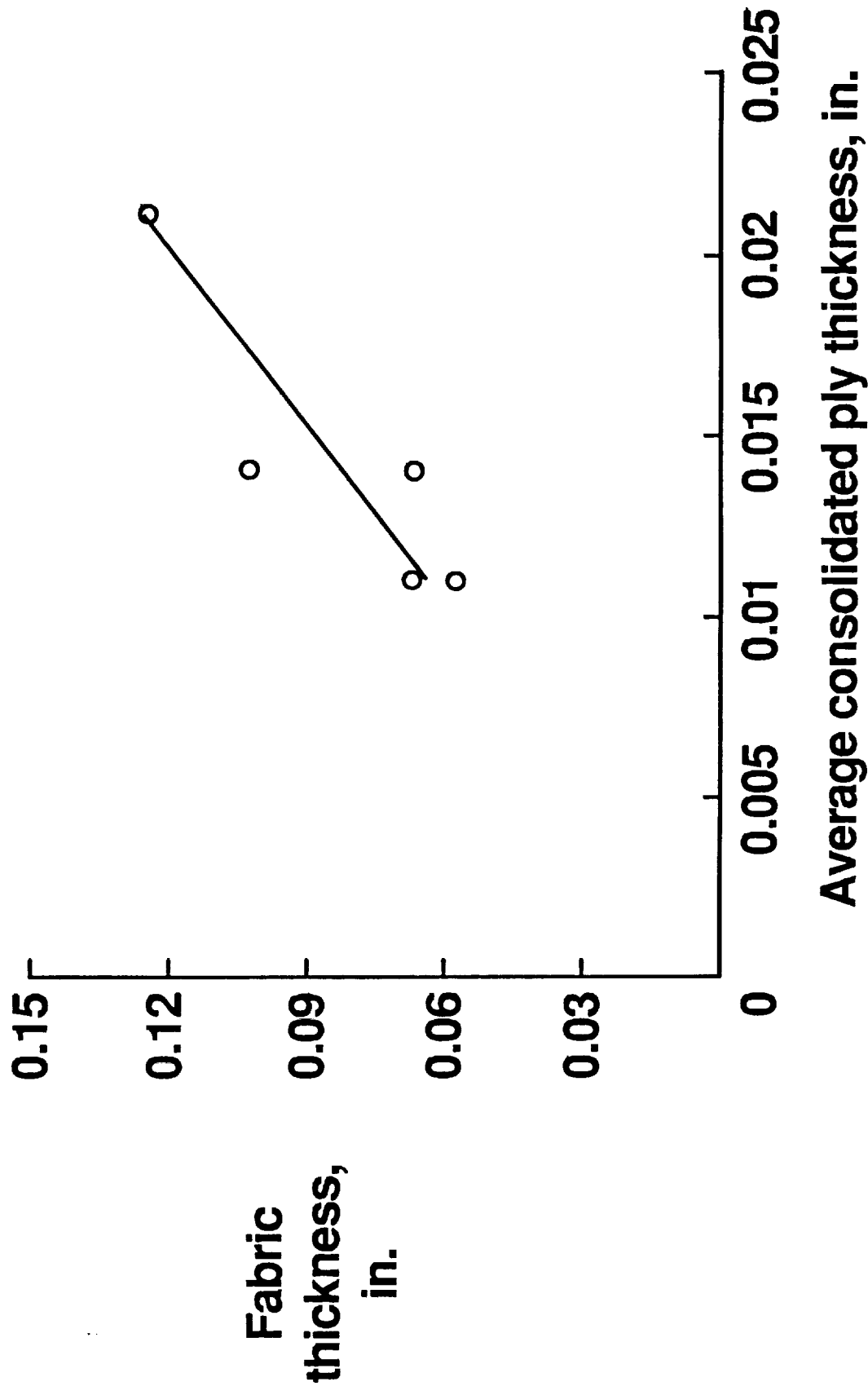


Using Twisted Towpreg



Using Non-twisted Towpreg

Bulk Factor Reduction on TTI 8HS Fabric



Net Shape Fabrication of Textile Preforms Using Powder-Coated Towpreg

- **Textile Architecture**
- **Tow Sizes**
- **Bulk Factor of Preform**
- **Resin**
- **Optimal Fiber Volume Fraction**

Accomplishments

- Established powder coating with thermoset and thermoplastic resins
- Determined weaving protocol and obtained good mechanical properties
- Developed towpreg customizing concepts

Future Direction

- Establish customized towpreg braiding protocol
- Fabricate net shape parts from powdered preforms
- Extend these techniques to new, high temperature performance materials